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Journal of Alloys and Compounds 434–435 (2007) 207–210

Journal of ALLOYS AND COMPOUNDS

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Free volume change in crystallization process of Zr–Cu–Al metallic glass studied by positron annihilation techniques

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Available online 9 October 2006

Abstract

Positron annihilation lifetime (PAL) and coincidence Doppler broadening (CDB) experiments have been performed to study free volume changes and atomic relaxation behavior in Zr–Cu–Al bulk metallic glass. $Zr_{50}Cu_{40}Al_{10}$ metallic glass was annealed isothermally at 673 K, which is below the glass transition temperature (T_g). During this annealing, PAL was observed to decrease, indicating a decrease in free volume; whereas, no significant change in CDB spectra was detected. This observation implies that the relaxation below T_g takes place without a change in atomic configuration. As for specimens annealed at 723 K ($>T_g$) for 100 s and subsequently annealed isothermally at 673 K for 18,000 s, PAL decreased similarly, suggesting a decrease in free volume. In addition, CDB spectra showed a systematic fluctuation of electron momentum distribution, especially in a high momentum region. This indicates that a chemical reordering took place during crystallization process.

Keywords: Amorphous materials; Electronic states; Positron spectroscopies

1. Introduction

The free volume of metallic glass has a significant effect on atomic relaxation and crystallization processes, although detailed atomic configurations and their motion around free volume site have not been clarified yet. The glass transition phenomenon is observed in all kinds of metallic glass. This transition behavior has been recognized to strongly depend upon the atomic rearrangement. It is also easy to control the structure through various kinds of heat treatment near the glass transition temperature. A dominant structural change of an amorphous phase prior to crystallization is relaxation to a stabler structure [1–3]. Many physical and mechanical properties, such as viscosity [4], atomic diffusivity [5], strength [6] are known to change during the relaxation process. Thus, understanding of the dynamics of atom migration and relaxation mechanism in bulk metallic glass is important for the application of materials to a variety of engineering problems.

Positron annihilation technique is a powerful tool, yielding atomic scale information, especially on vacancy type defects which are beyond the resolution limit of electron microscopy as positron annihilation parameters depend upon the electron density. Positron annihilation experiments have recently been applied to examine not only the vacancy type defects in metals and semiconductors but also the free volume changes associated with annealing, plastic flow and hydrogen charging of various compound amorphous alloys [7–9]. Moreover, positron-annihilation coincidence Doppler broadening (CDB) measurements provide information on changes in open volume as well as the detailed electron distributions around the site where positrons are annihilated. The local atomic element analysis has become possible by using CDB.

In our preliminary experiment crystallization did not take place after pre-annealing at a temperature slightly higher than T_g for a few seconds. Subsequently crystallization took place after long time annealing at a temperature below T_g. In this work, therefore, open volume changes including atomic and

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doi:10.1016/j.jallcom.2006.08.143

electronic structures for Zr–Cu–Al bulk metallic glass during this crystallization process have been studied by using PAL and CDB techniques.

2. Experimental procedure

$Zr_{50}Cu_{40}Al_{10}$ metallic glass (Ø8 mm × 60 mm) was prepared by the tilt casting method in an arc furnace [10,11]. The T_g of this glass is 675 K. Bulk of this material was cut into the size of Ø8 mm × 0.5 mm. A pair of specimens were annealed at 723 K ($>T_g$) for 100 s first, and subsequently annealed isothermally at 673 K for 300, 1000, 1800, 2800, 3600, 7200 and 18,000 s (including 100 s at723 K). At each annealing step, these samples were examined by PAL method using a conventional fast-fast circuit with the time resolution (FWHM) of about 200 ps and CDB experiments at room temperature. Each PAL and CDB spectrum consists of 1.5×10^6 and more than 10^9 counts, respectively. All of the PAL spectra were analyzed with RESOLUTION and POSITRONFIT programs developed at Risφ [12]. As a positron source we used 22-NaCl, which was sandwiched by thin sheets of Kapton foil and had an activity of about 300 kBq. The window for each *S*- and *W*-parameter was defined as $|p_L| < 5.0 \times 10^{-3}\ mc$ and $1.8 \times 10^{-2}\ mc < |p_L| < 2.5 \times 10^{-2}\ mc$ regions in the Doppler broadening spectrum in this case, respectively, where p_L is the electron momentum, c the speed of light and m is the electron rest mass. It is well established that change in S-parameter corresponds to the free volume change mainly, and the detailed profile at high electron momentum region (*W*-parameter) reflects the local structure and their atomic elements [13]. Specimens were examined by X-ray diffraction (XRD) measurements before and after annealing in order to identify their structures.

3. Results and discussion

3.1. XRD results

Change in XRD pattern of a $Zr_{50}Cu_{40}Al_{10}$ metallic glass with annealing is presented in Fig. 1. Crystallization did not take place after pre-annealing at 723 K for 100 s, and the amorphous phase remained after subsequent annealing at 673 K until 2 h later. After 5 h annealing, samples were crystallized completely same as those annealed at 773 K for 30 min. This is considered as follows: a short time annealing at a temperature slightly above T_g changes the structure of the meta-stable amorphous phase, then atom rearrangements, i.e., crystallization, takes place after long time annealing at a temperature slightly below T_g.

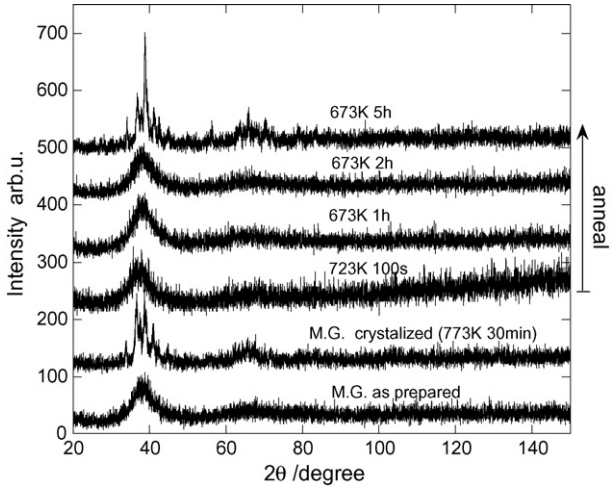

Fig. 1. XRD profiles of annealed $Zr_{50}Cu_{40}Al_{10}$ metallic glass first annealed at 723 K for 100 s then isothermally at 673 K. Also shown is the XRD profile of completely crystallized $Zr_{50}Cu_{40}Al_{10}$ alloy after 30 m at 773 K.

Table 1
Calculated [15] and experimental [14] values of positron lifetime in Al, Cu and Zr and their positron affinities A_+

	Bulk lifetime (ps)	Mono-vacancy (ps)	Positron affinity (eV)
Cu (fcc)	106, 120[a]	155	−4.81
Al (fcc)	166	253, 240[a]	−4.41
Zr (hex)	159, 165[a]		−3.98

[a] Experimental value.

3.2. Positron annihilation measurements

The positron lifetimes for as prepared amorphous and crystallized (fully annealed at 723 K for 5 h) $Zr_{50}Cu_{40}Al_{10}$ samples were 163 and 147 ps, respectively. The PAL of as prepared sample is similar to that of bulk Al and Zr materials [14] as shown in Table 1. It seems that all elements might be attracted to positron, because the differences of the positron affinity between Al, Cu and Zr [15] are not so big (e.g. $\Delta A_{+(\mathrm{Al–Cu})} = 0.4$ eV).

Fig. 2 shows the change in positron mean lifetime of a $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass annealed isothermally at 673 K after pre-annealing at 723 K for 100 s. Two-state trapping model, which assumes at least two kinds of trapping center (usually at vacancy type defects and free states in matrix) exist in the material, was applied for all of PAL data. In this case, however, analyzed PAL spectra were all in one component, namely, the positrons were trapped by only one type of open volume at each annealing step. After pre-annealing at 723 K the PAL decreases to 143 ps. This decreasing behavior reveals the reduction of open volume. This is in general agreement with the suggestion made by Nagel et al. for Zr–Al–Ni–Cu metallic glass alloy [16]. In contrast, no significant change is seen in XRD profiles until 10,000 s as shown in Fig. 1. Thus, the volume change is not accompanied by the crystallization. On the other hand, increasing of PAL from 143 to 161 ps by 300 s annealing at 673 K, which reflects increasing of open volume, was observed. This phenomenon is interesting but difficult to explain. We tentatively give the following interpretation for this result: Incomplete phase transition from one amorphous state to another more stable one

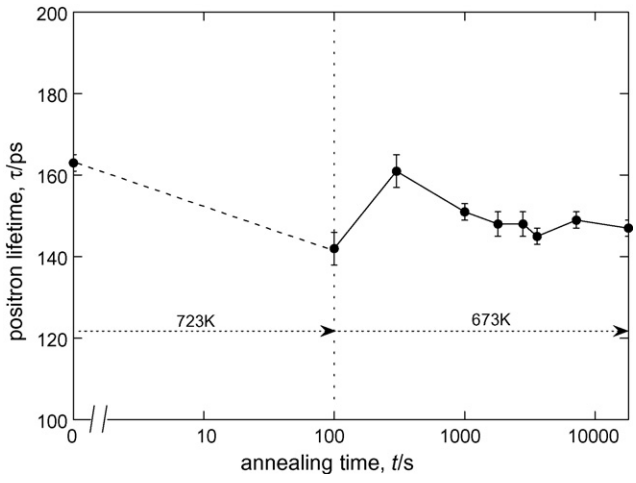

Fig. 2. Positron mean lifetime as a function of isothermal annealing at 673 K following annealing at 723 K for 100 s.

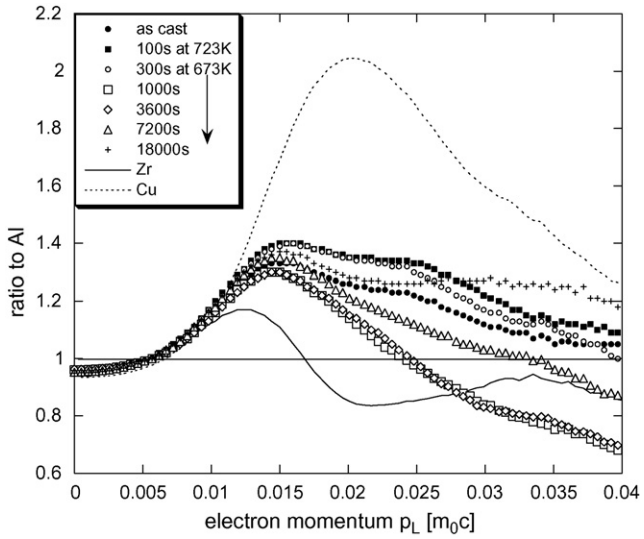

Fig. 3. CDB spectra of as prepared and annealed $Zr_{50}Cu_{40}Al_{10}$ metallic glasses together with those of Cu and Zr metals, shown as the ratio relative to that of Al metal.

with shrinking of open volumes have been caused by annealing a short period of time at a temperature above T_g, and then this open volume recovers again by subsequent annealing at a temperature below T_g.

Subsequent isothermal annealing at 673 K shows that PAL decreases gradually with increasing annealing time. XRD profiles (Fig. 1) show that crystallization does not occur yet after 2 h but occurs after 5 h annealing. These results demonstrate that structural relaxation, which is not accompanied by the crystallization, proceeds via decrease in free volume and finally crystallization takes place after 5 h annealing.

Fig. 3 shows that CDB spectra of $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass annealed isothermally at 673 K after pre-annealing at 723 K for 100 s, in the form of a ratio relative to the CDB spectrum of Al metal. For comparison, we also show the curves of the CDB ratio of Cu and Zr to Al. The CDB ratio profiles in the high momentum region suggest that the electronic structure of $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass is neither the same as that of Zr, Cu nor the same as Al. The annealing behavior of CDB profiles demonstrates interesting systematic fluctuation in a higher electron momentum region (>0.02 *mc*). We would like to focus attention on the change in the ratio in this electron momentum region. The CDB spectrum around 0.025 mc is first increased by pre-annealing at 723 K, decreases after annealing at 673 K, and finally goes up again after 18,000 s annealing. In order to extract possible changes in atomic and electronic structures around open volumes, *S*- and *W*-parameter as a function of annealing time are plotted in Fig. 4. The change in *S*-parameter does not correlate inversely with that in *W*-parameter, especially from 300 to 1800 s. The systematic change of *S*–*W* has been well established for another materials [13], and suggests that chemical environment of the site at which positrons annihilate does not alter. Further, the curve of the CDB ratio does not remain the same during annealing. Thus, chemical reordering continuously takes place throughout annealing. On the contrary, Yano et al.

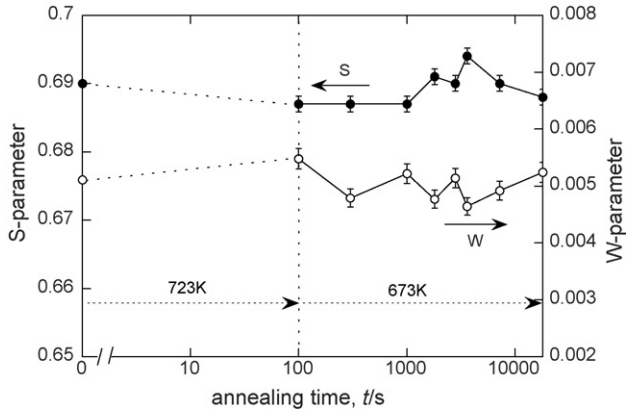

Fig. 4. Change in Doppler broadening *S*- and *W*-parameter during isothermal annealing.

[17] showed that for the same specimens annealed isothermally at 673 K without pre-annealing at 723 K, the CDB profile did not change during the structure relaxation process despite a marked decrease in PAL. They suggested both topologically and chemically invariance involving only shrinking of an open volume during atomic relaxation. Annealing behavior of PAL exhibited remarkable change at 100 s (723 K) and 300 s (673 K) as presented in Fig. 2. Correspondingly, the curve of the CDB ratio has a reverse trend after pre-annealing. This behavior suggests that not crystallization but structural relaxation accompanied by change in local chemical surroundings takes place by this heat treatment. Similarly, the chemical ordering in Zr–Ti–Al–Cu–Ni metallic glass during crystallization process was reported by Asoka-Kumar et al. [18].

Besides, the CDB profile rises up again with further annealing and its shape does not coincide with that after 18,000 s annealing, even though the value of PAL does not change considerably. Also the crystallization of $Zr_{50}Cu_{40}Al_{10}$ alloy was detected by XRD at 18,000 s. It follows from these results that mainly atomic reordering takes place during annealing time from 1000 to 18,000 s.

4. Conclusions

Free volume change in a crystallization process of $Zr_{50}Cu_{40}Al_{10}$ metallic glass has been studied by PAL and CDB techniques, and the following conclusions has been obtained: a stabler amorphous phase was induced in a bulk metallic glass by short time pre-annealing at a temperature slightly above T_g, and the atomic reconstruction occurs with a tendency to crystallization accompanied by shrinking of open volume during subsequent isothermal annealing under T_g. To discuss more detailed atomic configurations around open volumes, the calculation of positron annihilation in the amorphous phase is needed.

Acknowledgements

This study has been supported by a Grant-in-Aid for Scientific Research by the Ministry of Education, Culture, Sports, Science and Technology of Japan (Grant number 15074218).

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